PATENT SPECIFICATION

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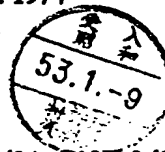
(54) PROCESS AND CATALYST FOR CONVERSION OF CARBON MONOXIDE AND STEAM TO HYDROGEN AND CARBON DIOXIDE

(71) We, EXXON RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Linden, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for producing hydrogen (and carbon dioxide) by reacting carbon monoxide with steam at elevated temperatures in the presence of a catalyst comprising at least one alkali metal compound and at least one metal hydrogenation-dehydrogenation component, and also to catalysts suitable for use in said process.

It is well known to prepare hydrogen by reacting carbonaceous materials, such as hydrocarbons with steam at elevated temperatures of 1200°—1400° F or coal or coke with steam at temperatures up to 2500° F, and then to react the resulting mixture of CO and H₂ with more steam at lower temperatures, for example, at 800°—900° F, in the presence of suitable catalysts to convert the carbon monoxide produced in the first stage to carbon dioxide and additional hydrogen. The second step, known as the water gas shift reaction, is limited by equilibrium considerations and complete conversion of CO to CO₂ is not realized. However, the concentration of CO in the product when equilibrium is reached is highly dependent on the temperature. Consequently, conversions can be increased by either removing the carbon dioxide and again contacting the CO and steam with the catalyst in the same or subsequent stages or by reducing the temperature.

The effect of temperature on the equilibrium constant

$$K = \frac{[CO_2][H_2]}{[CO][H_2O]}$$

is shown in the following table.

°F	K	Concentration of CO at Equilibrium (dry basis) Feed*	
		A	B
900	5.61	7.48	2.04
800	9.03	5.19	1.39
700	15.89	3.30	1.12
600	31.44	1.77	0.56
500	72.75	0.86	0.20
400	206.8	0.29	0.001

*A—50% of a 1/1 H₂/CO mixture + 50% H₂O (steam)
*B—30% of a 1/1 H₂/CO mixture + 70% H₂O (steam)

It is thus evident that less CO will remain unconverted and costly methods of operation will be avoided by operating at as low temperatures as possible, e.g. 200°—700° F. Such low temperatures can be employed by the use of a catalyst consisting of copper deposited on zinc oxide. Unfortunately, however, this catalyst will not tolerate even traces of sulfur in the feed.

It is known (see Canadian Patents 911,135 and 911,136) that gas mixtures containing carbon monoxide contaminated with relatively large amounts of sulfur can be converted to hydrogen economically by reaction with steam at reduced temperatures in the presence of a catalyst comprising (1) at least one alkali metal salt of an acid having an ionization constant less than about 1×10^{-3}, and (2) a hydrogenation - dehydrogenation component. The alkali metal compound (a compound of a Group IA element of the Periodic Table of Elements) and the hydrogenation-dehydrogenation component may be supported on an appropriate carrier. The Periodic Table of Elements referred to herein is in accordance with *Handbook of Chemistry and Physics* published by The Chemical Rubber Publishing Co., Cleveland, Ohio, 45th edition (1964). Suitable hydrogenation-dehydrogenation components include: (a) Group VIII noble metals, in particular, rhodium, ruthenium, palladium, osmium, iridium and platinum metals and compounds thereof; (b) rhenium; (c) non-noble metal materials including vanadium, molybdenum, cobalt, tungsten metals and compounds thereof including mixtures thereof, in particular, the oxides, sulfides or mixtures thereof; and (d) mixtures of one or more vanadium, molybdenum, cobalt and tungsten metals or compounds, preferably oxides, sulfides or mixtures thereof, with one or more nickel, iron or chromium materials, e.g., nickel, iron or chromium metals or compounds, preferably oxides, sulfides or mixtures thereof.

At least a portion of the non-noble catalyst species (categories (c) and (d) above) should exist in a sulfided form. Such catalysts are particularly suitable for use with feeds containing sulfur constituents. However, these catalyst compositions may also be used with sulfur-free feeds. When sulfur-containing feeds are used, the non-noble metal catalyst may be sulfided *in situ* by passing the feed over the oxide or other compound which is then converted at least partially to a sulfide. The noble metal containing catalysts are at least partially deactivated through contact with sulfur. Hence, these catalysts should be used with substantially sulfur-free feedstocks.

Maintaining the proper ratio of hydrogenation-dehydrogenation component to alkali metal compound in the catalyst is critical to its performance. Maximum catalyst activity is encountered when the ratio of hydrogenation-dehydrogenation component to alkali metal compound varies from 0.0001:1 to 10:1, the weight ratios being calculated on the basis of the oxides of each constituent. Preferably, the ratio of hydrogenation-dehydrogenation component to alkali metal compound (oxides thereof) is less than 5:1, most preferably less than 3:1. For purposes of calculating weight ratios, the metals are assumed to exist in only the following oxide forms: CoO, MoO_3, WO_3, V_2O_5, Fe_2O_3, NiO, Cr_2O_3, Ru_2O_3, Re_2O_7, RhO_2, PdO, Os_2O_3 and PtO_2.

Optimum process results are obtained when the particle size of the catalyst is about 1/32" or lower in diameter (spheres, cylindrical extrudates, etc.). Where the average catalyst particle size is larger such as, for example, $\frac{1}{8}$" diameter extrudates or $\frac{1}{4}$" diameter tablets, catalyst activity is reduced. Thus, the activity of a water gas shift reaction catalyst having a composition of 14 wt. % K_2CO_3, 3 wt. % CoO, 11 wt. % MoO_3 and 72% alumina support in the form of a $\frac{1}{8}$" diameter cylindrical extrudate has only 55.5% of the activity of a catalyst in the form of 20—40 U.S. standard screen mesh size particles.

The above-described process has proved quite satisfactory for many applications, but, in the interests of greater economy and efficiency, it is desirable to develop a shift reaction which would provide improved yields of hydrogen from carbon monoxide gas streams contaminated with sulfur and/or to effect additional cost savings.

In one aspect, the present invention provides a process for the conversion of carbon monoxide and steam to hydrogen and carbon dioxide, which comprises contacting a carbon monoxide and steam-containing reaction mixture in a reaction zone with a catalyst comprising (i) an alkali metal salt of an acid having an ionization constant less than 1×10^{-3} and/or an alkali metal compound which is at least partly convertible to the corresponding alkali metal carbonate during use of the catalyst in the conversion process and (ii) a hydrogenation - dehydrogenation component selected from (a) rhenium, (b) vanadium, molybdenum, tungsten, cobalt and mixtures thereof, or (c) vanadium, molybdenum, tungsten, cobalt or mixtures thereof admixed with nickel, iron, chromium or mixtures thereof, at least a portion of the hydrogenation-dehydrogenation component being in a sulfide form, the weight ratio of said hydrogenation-dehydrogenation component, calculated on the basis of the oxide thereof, to said alkali metal salt and/or compound, calculated on the basis of the oxide thereof, being in the range of from 0.0001:1 to 10:1, and (iii) a porous support having a surface area greater than 25 m²/g and a pore size distribution such that at least 50% of the total pore volume is in pores having diameters greater than 100

Angstroms, said contacting being conducted in the reaction zone at a temperature above the dew point temperature of the steam in the reaction mixture and in the range of from
5 200 to 700° F., and at a pressure below the dew point pressure (as herein defined) of the steam in the reaction mixture and in the range of from atmospheric pressure to 3000 psig, and at least a portion of said reaction zone
10 being maintained at a temperature between 30 and 70° F above the dew point temperature of said reaction mixture determined at the inlet of said reaction zone.

The dew point pressure is defined as the
15 pressure at which the partial pressure of water vapour is sufficient to initiate condensation of the water vapour, assuming ideal gas behaviour. For example, in a gas mixture consisting of 1 unit volume of dry gas and 1 unit
20 volume of steam at a temperature of 400° F, the partial pressure of saturated steam at 400° F is 247.31 psia. The dew point pressure is the pressure of the mixture at 400° F, i.e. $2 \times 247.31 = 494.62$ psia, assuming ideal gas
25 behaviour.

Preferably, at least a portion of the reaction zone is maintained at a temperature between 30 and 60° F, most preferably between 30 and less than 50° F above the dew
30 point temperature of the reaction mixture introduced into the reaction zone as measured at the reactor inlet. It has been discovered that when operating in this manner, the conversion of carbon monoxide and steam to
35 hydrogen is enhanced.

In commercial operations, the reaction mixture may also contain hydrogen and, in some instances, minor quantities of sulfur-bearing materials such as hydrogen sulfide.

40 In another aspect, the present invention provides a catalyst, suitable for use in promoting the conversion of carbon monoxide and steam to hydrogen and carbon dioxide, comprising (i) at least one alkali metal salt of an
45 acid having an ionization constant of less than 1×10^{-3} and/or an alkali metal compound which is at least partly convertible to the corresponding alkali metal carbonate when contacted with a gas mixture containing carbon
50 monoxide and steam at a temperature in the range of from 200 to 700° F and a pressure in the range of from atmospheric pressure to 3000 psig, and (ii) a hydrogenation-dehydrogenation component selected from (a)
55 rhenium, (b) vanadium, molybdenum, tungsten, cobalt or mixtures thereof, or (c) vanadium, molybdenum, tungsten, cobalt or mixtures thereof admixed with nickel, iron, chromium or mixtures thereof, at least a
60 portion of the hydrogenation-dehydrogenation component being in a sulfide form, the weight ratio of said hydrogenation-dehydrogenation component, calculated on the basis of the oxide thereof, to said alkali metal salt and/or com-
65 pound, calculated on the basis of the oxide

thereof, being in the range of from 0.0001:1 to 10:1, and (iii) a porous support having a surface area greater than 25 m²/g and a pore size distribution such that at least 50% of the total pore volume is in pores having diameters   70 greater than 100 Angstroms.

With this catalyst, substantially complete conversion of carbon monoxide to carbon dioxide, with concomitant production of hydrogen, occurs with even large catalyst   75 particle sizes. Suitable carriers include porous refractory inorganic oxides, such as alumina or various types, silica, silica-alumina, inter alia.

Suitable alkali metal catalyst components   80 include the carbonate, bicarbonate, biphosphate, sulfide, hydrosulfide, silicate, bisulfite, aluminate, hydroxide, tungstate, inter alia, of sodium, potassium, lithium, rubidium and cesium. In addition, the alkali metal salts of   85 organic acids, such as acetic acid, are equally suitable. Actually, the alkali metal salt of any acid which has an ionization constant of less than 1×10^{-3} may be used. Potassium and cesium salts, in particular potassium and   90 cesium carbonate, are most preferred.

It has been discovered that at least a portion of the weak acid alkali metal salts are converted to the corresponding alkali metal carbonate during the course of the shift re-   95 action. Additionally, salts of relatively unstable strong acids, such as nitric acid, are also converted, at least partially, to the carbonate. Hence, in most instances, the ultimate catalyst specie is believed to be the alkali   100 metal carbonate. Therefore, the alkali metal catalyst constituent may be any material that is at least partially converted to the alkali carbonate during the course of the shift reaction. Examples of useful hydrogenation-de-   105 hydrogenation metal catalyst components include molybdenum - chromium, tungsten-chromium, cobalt - nickel, cobalt - iron, molybdenum - tungsten, vanadium - tungsten, vanadium-cobalt, molybdenum, cobalt-iron,   110 nickel-tungsten, vanadium, cobalt-nickel-molybdenum, cobalt-iron-molybdenum and cobalt-molybdenum, inter alia.

If the above metal catalyst components are used with sulfur-containing feeds, they may   115 be initially employed in the form of the oxide or other compound easily sulfided. These compounds are then sulfided in situ during the passage of the sulfur-containing feed over them. Cesium or potassium carbonate or   120 acetate combined with cobalt-molybdenum oxides and/or sulfides is a particularly effective catalyst combination. The hydrogenation-dehydrogenation catalyst-components are herein referred to as the metals without   125 reference to how the or each metal is combined since if the actual composition, prior to the shift reaction is, for example, cobalt oxide-molybdenum oxide-aluminum oxide, under the reaction conditions, each metal   130

usually exists in a partially reduced and sulfided state which is difficult to define stoichiometrically and thus a description referring to the active metallic elements is as accurate as any.

Suitable catalyst support materials include aluminia materials such as gamma and alpha aluminas. Other suitable support materials include silica, silica-alumina, e.g., silica alumina cogel cracking catalysts; zeolites such as faujasite, erionite, and inter alia; activated carbon, coconut charcoal, magnesia, boria, thoria, titania and zirconia. Gamma and alpha-alumina catalyst supports are particularly preferred.

In a preferred embodiment, the catalytically active components are supported on a porous refractory inorganic oxide having the previously mentioned pore size distribution.

The extent of the surface area of the support material employed is believed to be a factor in the performance of the total catalyst system. The catalyst support should have a surface area greater than $25 . m^2/gram$, and usually, the support surface area will be between 25 and 500 $m^2/gram$, preferably between 25 and 400 $m^2/gram$, and most prefer-

ably between 50 and 300 $m^2/gram$, all as determined by the BET Method.

Critical to the improved catalyst of this invention is the pore size distribution of the catalyst support. At least 50% of the total pore volume being present must be in pores having diameters greater than 100 Å, and from a catalyst strength standpoint, it is desirable that from 50% to 95%, e.g. 50% to 85% of the total pore volume, and most preferably from 50% to about 80% of the total pore volume, will be in pores having diameters greater than 100 Å. Pore size distribution is measured by nitrogen adsorption techniques wherein the volume of nitrogen adsorbed on the support is measured at various pressures. This technique is more fully described in an article by Ballou et al, *Analytical Chemistry 32*, 532—36 (1960). Other techniques that give results that are consistent with this method can be used.

The pore size characteristics of the support material may also be expressed in terms of surface area, pore volume and average pore diameter. The preferred, more preferred and most preferred ranges are as follows:

	Surface Area m²/gram	Pore Vol. ml/gram	Av. Pore Diam., A
preferred	25—500	0.10—1.0	80—300
more preferred	25—400	0.15—0.90	90—250
most preferred	50—300	0.20—0.80	100—200

Average pore diameter is calculated according to the following formula:

$$\frac{4 \times \text{Total Pore Volume} \times 10^4}{\text{Total Surface Area}}$$

The catalyst components can be incorporated on the support in any conventional manner. Preferably, the hydrogenation-dehydrogenation components are placed on the support first and this combination is then calcined, e.g., at 1000°—1200° F., to convert the metals to the stable oxide forms. Then the alkali metal material, e.g., cesium or potassium carbonate, is impregnated onto the support using aqueous or alcoholic media and the catalyst dried. The alkali metal constituent impregnation operation can be carried out before the catalyst is introduced into the reactor or after the unfinished catalyst is placed within the reaction zone. In general, the support material is impregnated with a solution containing the desired compound. The finished catalyst is then sulfided in a known manner, e.g., by passing over the catalyst a mixture of hydrogen and hydrogen sulfide,

carbon disulfide or butyl mercaptan, inter alia. However, it may be sulfided *in situ* as described above.

The hydrogenation-dehydrogenation component is generally used in amounts varying from 0.0001 to 10 parts by weight based on the alkali metal compound, calculated as the oxide. The metal constituent/alkali metal compound weight ratio preferably varies from 0.01 to 5.0 parts by weight of hydrogenation-dehydrogenation material and, most preferably, from 0.1 to 3.0 parts by weight of metal catalyst per part by weight of alkali metal compound, exclusive of any support which might be used to support either or both components. All components are calculated on the basis of the oxide thereof.

The amount of catalyst components (metal material and alkali compound) present relative to the support may range from 50 to 1

wt. %, preferably from 40 to 2 wt. %, all based on total catalyst including the support. Catalysts which have been found particularly effective contain a mixture of cobalt and molybdenum materials contained on gamma alumina. Particularly effective supported catalysts contain a mixture of from 0.1 to 10 wt. % cobalt material and from 1 to 25 wt. % molybdenum material, preferably from 1 to 5 wt. % cobalt material and from 5 to 15 wt. % molybdenum material.

The shift process is preferably carried out continuously. The gaseous hourly space velocity can vary within wide limits. Gaseous hourly space velocities of at least 300 volumes of feed per volume of supported catalyst per hour (V/V/Hr), preferably space velocities between about 300 and 30,000 (V/V/Hr), measured on the basis of dry gas under standard conditions are particularly suitable for most applications. The process may be carried out at higher gaseous hourly space velocities if desired.

In the preferred modes of practice of this invention, carbon monoxide or a gas containing 0.1% or more carbon monoxide by volume, and steam in an amount of 1—100 volumes per volume of carbon monoxide, are passed over the catalyst in a reaction zone at a temperature above the dew point temperature of the steam in the reaction mixture and in the range of from 200° and 700° F. The pressure in the reaction zone is maintained below the dew point pressure of the steam in the reaction mixture and is preferably from 200 to 1500 psig.

In a typical commercial environment, the shift catalyst is maintained as a fixed bed within one or more reactors. As noted earlier, maximum catalyst performance is obtained when the reaction zone is maintained at a temperature in the range of from 30 to 70° F above the dew point temperature of the reaction mixture issuing into the reaction zone, in accordance with a feature of the invention. When the reaction is carried out adiabatically, it is not normally possible to maintain the entire volume of the reaction zone at a temperature varying from 30 to 70° above the dew point temperature of the inlet reaction mixture because of the exothermic nature of the shift reaction. When the reaction is carried out in an adiabatic system, it is desirable to adjust reactor configurations and catalyst loadings in order to secure the maximum amount of reactor volume that is maintained within the desired temperature range above the dew point temperature of the inlet reaction mixture. In some instances, this result can be obtained by utilizing reactors containing a plurality of small catalyst beds with provision for cooling between each catalyst bed. The catalyst may be used in an isothermal system wherein the catalyst is maintained in tubes that are surrounded by a heat transfer medium. The process is particularly effective when the carbon monoxide-containing feed gas contains a sulfur constituent. In fact, the presence of a sulfur material in the feed actually results in increased conversions in many cases. If necessary, the catalyst may be regenerated by oxidation and resulfiding.

The use of the catalyst of this invention leads to an extremely high heat release. Heat control may therefore be an important consideration in designing process equipment. Heat problems may be avoided with the use of a fluidized process in place of the fixed bed process normally used for a shift reaction. If a fixed bed process is used, the high heat release might be accommodated by the use of an inert diluent or by pseudo staging of the beds by diluting the catalyst along the length of the catalyst beds.

The invention is now further described with reference to some non-limitative Examples thereof and with reference to the single figure of the accompanying drawings which shows the data of Example 1 in graphical form.

EXAMPLE 1.

A series of tests were conducted to demonstrate the improvement in performance obtained with a shift reaction catalyst comprising a hydrogenation-dehydrogenation component in combination with an alkali metal constituent when the shift reaction is conducted at temperatures varying from 30 to 70° above the dew point of the inlet reaction mixture. The base catalyst employed in the tests consisted of about 15.7 weight percent potassium carbonate, 2.95 weight percent CoO, 10.54 weight percent MoO, and the balance alumina. The base catalyst, in 20—40 U.S. standard screen mesh size particles, was presulfided prior to use by contact with a hydrogen sulfide-containing gaseous mixture at elevated temperature and pressure conditions.

A 30 cubic centimeter charge of the sulfided catalyst was loaded into a steel reactor having a 30 cubic centimeter capacity and 10/1 length to diameter ratio. The reactor was maintained at constant temperature by a surrounding fluidized sand bath. Each of the experiments were carried out at a constant reaction zone temperature of 300° F and reaction zone pressure of 27 psig. The total dry gas plus steam feed rate was maintained constant so as to maintain a constant contact time of 1.35 seconds. Steam was provided to the system by pumping a predetermined amount of demineralized water into a reactor inlet. The dry feed gas consisted of about 88.2 volume percent hydrogen, 11.0 volume percent carbon monoxide and about 0.8 percent hydrogen sulfide. Variations in the dew point of the inlet reaction mixture were

secured by adjusting the ratios of steam to dry feed gas in the inlet mixture. In every instance a molar excess of steam was used.

The flow rates employed for various operational periods, the carbon monoxide conversion secured and the difference between reaction zone temperature and the dew point temperature of the inlet mixture for each of the tests are recorded in Table I below. The data are also plotted versus approach to dew point in the single figure of the accompanying drawings. The relative activity values plotted in the figure were assigned by comparing the reaction rates encountered at the given conditions assuming a first order reaction rate with respect to carbon monoxide conversion.

TABLE I

Test	Exit Dry Gas Rate (Liters/Minute at Room Temperature and Pressure Conditions)	Steam Feed Rate (cc. H₂O/Minute)	Co Conversion (%)	Reaction Zone Temperature (°F Above Dew Point of Inlet Mixture)
1	2.35	0.25	6.0	135
2	2.05	0.48	9.3	107
3	1.74	0.70	13.8	88
4	1.54	0.85	19.7	78
5	1.12	1.15	33.8	62
6	0.71	1.45	68.7	48
7	0.51	1.60	90.4	43
8	0.30	1.75	99.2	38

The data in Table I illustrates the remarkable improvement in carbon monoxide conversion and catalyst activity obtained by operating the water gas shift process at temperatures varying from about 30 to 70° F above the dew point of the inlet reaction mixture.

EXAMPLE 2.

Tests were carried out to compare the effectiveness of the catalyst of the present invention with a catalyst whose support exhibited a pore size distribution with less than 50% of the total pore volume being present in pores having diameters greater than 100 Å.

Catalyst A consisted of 14.9 wt. % potassium carbonate, 3.0 wt. % CoO and 10.6 wt. % MoO₃ on alumina in the form of ⅛" diameter, cylindrical extrudates. Catalyst B consisted of 22.6 wt. % potassium carbonate, 2.7 wt. % CoO and 9.7 wt. % MoO₃ on alumina in the form of ⅛" diameter spheres. Both catalysts were prepared by impregnating an alumina/CoO/MoO₃ composite with potassium carbonate. In the test, 45 cubic centimeters of each catalyst, diluted to 100 cubic centimeters with 20 to 40 mesh alpha alumina, was packed within a one inch inside diameter tubular reactor. Even though Catalyst B contained greater quantities of potassium carbonate, the reactor, in each test, contained substantially identical amounts of carbonate (0.118 g/cc of reactor volume for Catalyst A versus 0.119 g/cc of reactor volume for Catalyst B because of differences in the packed density of the two catalysts. A feed stock comprising 50 volume percent hydrogen, 49 volume percent carbon monoxide and 1 volume percent hydrogen sulfide and steam was passed over the catalyst at a rate sufficient to produce a space velocity of 2420 volumes of dry product gas per actual volume of catalyst per hour. Steam was introduced into the reaction zone at a rate of 1.03 moles per mole of dry product gas. The shift conversion reaction was conducted at a temperature of about 400° F. and a reaction zone pressure of about 100 psig. The results of the tests are set forth in Table II below.

TABLE II

	Catalyst A	Catalyst B
Surface area, m²/gm(a)	269	270
Pore volume, ml/gm(a)	0.48	0.729
Pore volume in diameters greater than 100 A, ml/gm(a)	0.19	0.398
% Pore volume in pores greater than 100 A	39.6	54.8
Average pore diameter, Å	71.5	108
Activity		
CO conversion, %	75.1	98.7
relative activity(b)	1	3.2

(a) Determined prior to potassium carbonate impregnation.
(b) Calculated assuming a first order reaction rate with respect to CO conversion.

The data set forth in Table II demonstrate the improved result secured with the improved catalyst of the present invention.
5 Although a minor portion of the relative activity superiority of Catalyst B over Catalyst A may be attributed to the higher effectiveness of spherically shaped catalysts versus extrudate catalysts, Catalyst B,
10 nevertheless, is substantially more active than Catalyst A even though it contained substantially less hydrogenation-dehydrogenation component than Catalyst A.

Attention is drawn to U.K. patent speci-
15 fication 1,281,051 which describes and claims a process for the conversion of a gas mixture containing carbon monoxide and steam to hydrogen and carbon dioxide which comprises contacting the gas mixture at a temperature
20 of at least 300° F with a composition for catalyzing the conversion, said composition comprising (1) at least one alkali metal compound derived from an acid having an ionization constant of less than 1×10^{-3} and (2) a
25 hydrogenation - dehydrogenation component comprising ruthenium, palladium, osmium, iridium or platinum, or comprising one of vanadium, molybdenum, tungsten or cobalt, or mixtures comprising iron or nickel and/or
30 cobalt with molybdenum, chromium, tungsten or vanadium, the weight ratio of the hydrogenation-dehydrogenation component to the alkali metal compound calculated on the basis of their respective oxides, being in the range
35 of from 0.001:1 to 10:1.

Attention is also drawn to UK patent specification 1,388,061 which describes and claims a process for catalyzing the conversion of a gas mixture containing carbon monoxide and
40 steam to carbon dioxide and hydrogen, com-
prising contacting the gas mixture at a temperature of at least 300° F with a composition comprising a mixture of (1) at least one alkali metal compound of an acid having an ionization constant of less than 1×10^{-3} and
45 (2) a hydrogenation-dehydrogenation component comprising a mixture of vanadium with molybdenum or tungsten, or a mixture of molybdenum with chromium or tungsten, or a mixture of cobalt with iron, or comprising
50 chromium, the weight ratio of the hydrogenation-dehydrogenation component to the alkali metal compound, calculated on the basis of their respective oxides, being in the range of from 0.001:1 to 10:1.
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WHAT WE CLAIM IS:—

1. A process for the conversion of carbon monoxide and steam to hydrogen and carbon dioxide, which comprises contacting a carbon monoxide and steam-containing reaction mix-
60 ture in a reaction zone with a catalyst comprising (i) an alkali metal salt of an acid having an ionization constant less than 1×10^{-3} and/or an alkali metal compound which is at least partly convertible to the
65 corresponding alkali metal carbonate during use of the catalyst in the conversion process and (ii) a hydrogenation-dehydrogenation component selected from (a) rhenium, (b) vanadium, molybdenum, tungsten, cobalt and
70 mixtures thereof, or (c) vanadium, molybdenum, tungsten, cobalt or mixtures thereof admixed with nickel, iron, chromium or mixtures thereof, at least a portion of the hydrogenation-dehydrogenation component being in
75 a sulfide form, the weight ratio of said hydrogenation-dehydrogenation component, calculated on the basis of the oxide thereof, to said

alkali metal salt and/or compound, calculated on the basis of the oxide thereof, being in the range of from 0.0001:1 to 10:1, and (iii) a porous support having a surface area greater than 25 m²/g and a pore size distribution such that at least 50% of the total pore volume is in pores having diameters greater than 100 Angstroms, said contacting being conducted in the reaction zone at a temperature above the dew point temperature of the steam in the reaction mixture and in the range of from 200 to 700° F., and at a pressure below the dew point pressure (as herein defined) of the steam in the reaction mixture and in the range of from atmospheric pressure to 3000 psig, and at least a portion of said reaction zone being maintained at a temperature between 30 and 70° F above the dew point temperature of said reaction mixture determined at the inlet of said reaction zone.

2. The process of claims 1 conducted at a pressure of from 200 to 3,000 psig and at a space velocity of at least 300 volumes of reaction mixture per volume of supported catalyst per hour.

3. The process of claim 1 or claim 2 wherein said support is a refractory inorganic oxide having a pore size distribution such that from 50% to 95% of the total pore volume is in pores having diameters greater than 100 Angstroms.

4. The process of claim 3 wherein said support has a pore size distribution such that from 50 to 85% of the total pore volume is in pores having diameters greater than 100 Angstroms.

5. The process of any one of claims 1 to 4 wherein said alkali metal salt is an alkali metal carbonate.

6. The process of any one of claims 1 to 5 wherein said reaction mixture contains a sulfur material.

7. The process of any one of claims 1 to 6 wherein said support is alumina.

8. A process for the conversion of carbon monoxide and steam to hydrogen and carbon dioxide according to any one of claims 1 to 7 substantially as hereinbefore described.

9. Hydrogen and/or carbon dioxide obtained by the conversion process of any one of claims 1 to 8.

10. A catalyst, suitable for use in promoting the conversion of carbon monoxide and steam to hydrogen and carbon dioxide, comprising (i) at least one alkali metal salt of an acid having an ionization constant of less than 1×10^{-3} and/or an alkali metal compound which is at least partly convertible to the corresponding alkali metal carbonate when contacted with a gas mixture containing carbon monoxide and steam at a temperature in the range of from 200 to 700° F and a pressure in the range of from atmospheric pressure to 3000 psig, and (ii) a hydrogenation-dehydrogenation component selected from (a) rhenium, (b) vanadium, molybdenum, tungsten, cobalt or mixtures thereof, or (c) vanadium, molybdenum, tungsten, cobalt or mixtures thereof admixed with nickel, iron, chromium or mixtures thereof, at least a portion of the hydrogenation-dehydrogenation component being in a sulfide form, the weight ratio of said hydrogenation-dehydrogenation component, calculated on the basis of the oxide thereof, to said alkali metal salt and/or compound, calculated on the basis of the oxide thereof, being in the range of from 0.0001:1 to 10:1, and (iii) a porous support having a surface area greater than 25 m²/g and a pore size distribution such that at least 50% of the total pore volume is in pores having diameters greater than 100 Angstroms.

11. The catalyst of claim 10, in which said support has a pore size distribution such that from 50% to 95% of the total pore volume is in pores having diameters greater than 100 Angstroms.

12. The catalyst of claim 10 or claim 11, wherein said alkali metal salt is an alkali metal carbonate.

13. The catalyst of claim 12, wherein said alkali metal carbonate is potassium carbonate.

14. The catalyst of any one of claims 10 to 13 wherein said hydrogenation-dehydrogenation component comprises a sulfided mixture of cobalt and molybdenum.

15. The catalyst of any one of claims 10 to 14 wherein said support is alumina.

16. A catalyst according to any one of claims 10 to 15 substantially as hereinbefore described.

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